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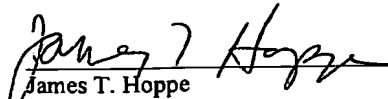
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PROVISIONAL APPLICATION COVER SHEET

| | | | | |
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| TITLE OF THE INVENTION (280 characters max) | | | | |
| STABILIZED POLYETHYLENE MATERIAL | | | | |
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| ENCLOSED APPLICATION PARTS (check all that apply) | | | | |
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PROVISIONAL APPLICATION FILING ONLY

STABILIZED POLYETHYLENE MATERIAL

FIELD OF THE INVENTION

The present invention relates to stabilized polyethylene resin and in particular a stabilized multimodal polyethylene resin as well as compositions containing such resin. The present invention also relates to applications of such resin or composition, for example to make a shaped article. The resin and composition of the invention are particularly suitable for use in pipes.

10 BACKGROUND AND SUMMARY OF THE INVENTION

Polyethylene is known for use in shaped articles including pipes. Polyethylene compositions with a multimodal molecular weight distribution (MWD), for example a bimodal MWD, can offer distinct advantages compared with unimodal polyethylenes or other polyolefins. For example, bimodal polyethylenes may combine the favorable mechanical properties afforded by a high molecular weight polyethylene with the good processability of a low molecular weight polyethylene. The prior art reports that such materials can advantageously be employed in various applications, including film or pipe applications. Prior art multimodal polyethylenes suggested for use in pipes include the materials disclosed in the PCT applications with the publication numbers WO 97 /29152, WO 00/ 01765, WO 00/18814, WO 01/02480 and WO 01/25328.

In view of the potentially disastrous consequences of material failures, acceptance of any plastic pipe for water or gas distribution is subject to product standards and performance requirements set forth in norms, for example, DIN (German Industrial Norm or "Deutsche Industrie Norm") or norms defined by ISO (International Organization for Standardization, Geneva, Switzerland). For example, state of the art polyethylene materials sold into pipe applications, such as irrigation pipes, sewage pipes, domestic pipes (including under floor heating, snow melt systems, hot and cold water delivery) or pressure pipes, meet the so-called PE80 or PE100 ratings (PE stands for polyethylene). Pipes manufactured from polyethylenes classifying as PE80-type or PE100-type resins must withstand a minimum circumferential stress, or hoop stress, of 8 MPa (PE80) or 10 MPa (PE100) at 20°C for 50 years. PE100 resins are high density polyethylene (HDPE) grades typically having a density of at least about 0.950 g/ccm³ or higher.

Their relatively poor Long Term Hydrostatic Strength (LTHS) at high temperatures has been an acknowledged disadvantage of traditional polyethylenes which rendered these materials unsuitable for use in piping with exposure to higher temperatures, such as domestic pipe applications. Domestic pipe systems typically operate at pressures between about 2 and about 10 bar and temperatures of up to about 70°C with malfunction temperatures of about 95 - 100°C. Domestic pipes include pipes for hot and/or cold water in pressurized heating and drinking water networks within buildings as well as pipes for snow melt or heat recovery systems. The performance requirements for the various classes of hot water pipes, including underfloor heating, radiator connectors and sanitary pipes are specified, for example, in International Standard ISO 10508 (first edition October 15, 1995, "Thermoplastic pipes and fittings for hot and cold water systems").

In many applications chlorine is added to the water to be used as a disinfectant. Chlorinated water systems present additional challenges for plastic pipe systems, as chlorine exposure is known to increase failure rates (that is, less time is needed until a leak is detected. It is known that chlorine reacts with polyethylene in an oxidation-reduction reaction resulting in the polymer degradation. Antioxidants are typically used to counter the effect of chlorine, but it has been discovered that conventional anti-oxidants used with resins currently used in pipe applications can be extracted by the water in a relatively short period of time.

Accordingly, there is still the need for new stabilized polyethylene materials which offer an advantageously balanced combination of thermal, mechanical and processing properties, and which maintain their physical properties in chlorinated water environments. It is an object of the present invention to meet these and other needs.

It has been discovered that at least three factors effect the stability of plastic pipes used with chlorinated water systems. First, the exterior of the pipes is exposed to oxygen in the air. Second the interior of the pipes are exposed to chlorine in the water. Antioxidants can be used to increase the resistance of the pipe to either of these factors, however it has been discovered that each antioxidant is not equally effective against each of these environmental factors. Another factor which was observed to have a relationship to the long term stability of pipes in chlorinated water systems, is the ability of the antioxidants to resist extraction from the water from the interior of the pipe. Currently there are no known

antioxidant systems which satisfactorily address the combination of all of these factors for standard polyethylene resins.

Accordingly, the present invention provides a class of resins which shows an increased affinity towards additives in that the additives are less likely to be extracted in a water-containing environment. The present invention also provides a particular combination of antioxidant additives which demonstrate a synergistic effect in lengthening the oxidation induction time for plastic pipes in a chlorinated water systems.

The preferred resin for use in present invention is a polyethylene resin with a density in the range of from about 0.925 g/cc to about 0.965 g/cc, with densities above about 0.940 g/cc being most preferred. The resin should also have a melt index (I_2) in the range of from about 0.05 g/10 minutes to about 5 g/10 minutes, more preferably in the range of 0.1 to 1 g/10 minutes.

The antioxidant additives of the present invention comprise at least two antioxidants which operate synergistically for the environment of a pipe for use with a chlorinated water supply. Accordingly, one of the antioxidants should be chosen for its performance with respect to the atmosphere external to the pipe, and another antioxidant should be chosen for its performance with respect to chlorine exposure in the interior of the pipe. Preferred antioxidants include hindered phenols, phosphites and phosphonites.

The present invention also relates to applications of such formulated polyethylene resin and composition and to shaped articles such as pipes, made from such polyethylene resin or composition.

DETAILED DESCRIPTION OF THE INVENTION

Basic definitions

The term "interpolymer" is used herein to indicate polymers prepared by the polymerization of at least two monomers. The generic term interpolymer thus embraces the terms copolymer, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different monomers, such as terpolymers.

Unless indicated to the contrary, all parts, percentages and ratios are by weight. The abbreviation "ccm" stands for cubic centimeters.

Unless expressly specified otherwise, the term "melt index" means the I_2 melt index, as determined in accordance with ASTM D1238 under a load of 2.16 kg and at a temperature of 190°C.

Unless specified otherwise, the term "alpha-olefin" (α -olefin) refers to an aliphatic or cyclo-aliphatic alpha-olefin having at least 4, preferably from 4 to 20 carbon atoms.

The present invention provides a polyethylene resin with a density of at least about 0.925 g/cc, more preferably about 0.930 g/cc, most preferably about 0.940g/cc. The polyethylene resin can have a maximum density of about 0.965 g/cc.. The resin should also have a melt index (I_2) in the range of from about 0.05 g/10 minutes to about 5 g/10 minutes, more preferably in the range of 0.1 to 1 g/10 minutes. The resin can also advantageously have a multimodal molecular weight distribution. Preferred resins for use in the present invention, and suitable processes for making them are taught in WO 03/020821, which is hereby incorporated by reference in its entirety. The resins used in the present invention may be crosslinked according to methods known in the art, but this is not required.

While not intending to be bound by theory, it is hypothesized that the higher density materials achieve better results because of their crystalline structure. The higher the density of the material the less amorphous regions it contains. It is believed that water can penetrate these amorphous regions and extract antioxidant located there, whereas the water cannot penetrate the crystalline regions. Thus, the higher density materials offer less areas from which the antioxidants may be extracted, resulting in higher concentration of antioxidant material over time. It should be noted that this effect improves the performance of all antioxidants and not just the preferred combination of antioxidants of the present invention. It will readily be understood by those skilled in the art that this beneficial effect of reducing antioxidant extraction observed when using the high density material does not counter other physical limitations of high density materials, such as generally poorer toughness and flexibility. Thus the particular resin used should be optimized for the needs of a particular application

The present invention also provides compositions comprising the high density polyethylene resin of the invention and an antioxidant package comprising at least two antioxidant additives. It was discovered that antioxidants do not respond to different elements equally. Thus, some antioxidants are better at preventing deterioration of a pipe when exposed to air, whereas others may be better at preventing deterioration of the same

pipe when exposed to chlorine. Accordingly, for the present invention, one antioxidant additive should be selected for its efficacy as an antioxidant when exposed to air, and the other antioxidant additive should be chosen for its efficacy when exposed to chlorine. The choice of antioxidant may also change depending on whether the resin is to be cross-linked.

5 For efficacy against exposure to air, it was discovered that hindered phenols such as Irganox™ 1330 are preferred. For efficacy against chlorine exposure hindered phenols such as Irganox™ 1010 or Irganox™ 1076 are preferred. Thus, for use in pipes intended for use with chlorinated water, an additive package with efficacy against air and chlorine is preferred.

10 Other additives may also be added to the resin or the antioxidant package, including still other antioxidants which may be more effective at preventing oxidation at higher temperatures which the resin may be exposed to during extrusion. Such antioxidants include phosphites and phosphonites such as Irgafos™ 168. Metal deactivators such as Irganox™ MD 1024 and Naugard™ XL1, processing aids, UV stabilizers, other
15 antioxidants, pigments or colorants can also be advantageously used with the compositions of the present invention.

When used to make pipes for use with chlorinated water, the resin of the present invention contains hindered phenols such as Irganox™ 1330, hindered phenols such as Irganox™ 1010 and/or Irganox™ 1076, phosphites such as Irgafos 168 and metal
20 deactivators such as Irganox™ MD 1024 and/or Naugard™ XL1.

The resins or compositions of the present invention can be used to manufacture a shaped article. Such article may be a single-layer or a multi-layer article, which is obtainable by suitable known conversion techniques applying heat, pressure or a combination thereof to obtain the shaped article. Suitable conversion techniques include, for example, blow-
25 molding, co-extrusion blow-molding, injection molding, injection stretch blow molding, compression molding, extrusion, pultrusion, calendering and thermoforming. Shaped articles provided by the invention include, for example, films, sheets, fibers, profiles, moldings and pipes.

The polyethylene resins and compositions according to the present invention are
30 particularly suitable for durable application, especially pipes - without the need for cross-linking. Pipes comprising polyethylene resin as provided herein are another aspect of the present invention and include monolayer pipes as well as multilayer pipes, including

multilayer composite pipes. The pipes of the invention comprise the high density polyethylene resin in form of a composition (formulation) which also contains the antioxidant package of the present invention, and optionally other additives or fillers.

Monolayer pipes according to the present invention consist of one layer made from a composition according to the present invention comprising a high density polyethylene resin together with an antioxidant package as provided herein and any additional suitable additives typically used for pipe applications. Such additives include colorants and materials, such as, for example, process stabilizers, pigments, metal de-activators, and UV protectors.

Multilayer composite pipes comprising one or more, e.g., one or two, layers wherein at least one layer comprises a composition according to the present invention, are also possible. In such cases the high density resin should be used at least for the inner layer as this is the layer which is exposed to the water. It should be understood that in a multilayer pipe, the antioxidant package used with the high density resin may be different and the resin may not be exposed to air. Such multilayer pipes include, for example, three-layer composite pipes with the general structure PE/Adhesive/Barrier, or five-layer pipes with the general structure PE/Adhesive/Barrier/Adhesive/PE or Polyolefin/Adhesive/Barrier/Adhesive/PE. In these structures PE stands for polyethylene layers which can be made from the same or different polyethylene compositions. Suitable polyolefins include, for example, high density polyethylene, polypropylene and polybutylene, homopolymers and interpolymers. The barrier layer may be an organic polymer capable of providing the desired barrier properties, such as an ethylene-vinyl alcohol copolymer (EVOH), or a metal, for example, aluminum or stainless steel.

The invention is further illustrated by the following Examples, which, however, shall not be construed as a limitation of the invention.

Examples

Various resin formulations were prepared by first blending a masterbatch containing additives to a base resin in order to achieve the additive levels specified in Table 1. For examples 1-8 the base resin was an ethylene/octene resin with a density of 0.941 g/cc and a melt index (I_2) of 0.85 (determined according to ASTM D-1238, condition E, 190°C/2.16 kg). For Example 9 the base resin was polyethylene resin having a density of 0.933 and a

melt index (I_2) of 0.7. For Example 10, the base resin was a polyethylene resin having a density of 0.9345 g/cc and a melt index (I_2) of 0.6. In Table 1, AO 1 is Irganox™ 1330, a hindered phenol antioxidant; MD is a metal deactivator, (Naugard™ XL1 for Examples 1,3,4,6,8, and 9 and Irganox™ MD1024 for Examples 2 and 5); AO2 is Chimassorb™ 944 a hindered amine antioxidant; AO3 is Irgafos™ 168, a phosphite antioxidant; AO4 is Irganox™ 1010, a hindered phenol antioxidant ; and AO5 is Irganox™ 1076, a hindered phenol .

The formulated resins were then extruded at commercial pipe extrusion lines to make pipes having a 17 mm (except for Example 9 which was 16 mm and Example 10 which was 16mm) outer diameter and a 2 mm thickness. These pipes were evaluated for chlorine resistance according to Jana Laboratories Procedure APTF-2, and the time until failure is reported in the last column of Table 1. The testing conditions were as follows: pH 6.8 (± 0.1); Chlorine 4.1 mg/L (± 0.1); Nominal ORP 830mV; fluid temperature 110°C (± 1); air temperature 110°C (± 1); pressure 70 psig (± 1); flow rate 0.1 Us gallons/min ($\pm 10\%$)

| Sample | AO1 | MD | AO2 | AO3 | AO4 | AO5 | F time (hr) |
|--------|------|-----|------|------|------|-----|-------------|
| 1 | 2329 | 621 | 0 | 960 | 0 | 399 | 1473 |
| 2 | 2373 | 648 | 0 | 959 | 0 | 422 | 1088 |
| 3 | 2207 | 644 | 32.4 | 930 | 0 | 413 | 1531 |
| 4 | 0 | 500 | 0 | 1085 | 0 | 401 | 841 |
| 5 | 0 | 815 | 0 | 1099 | 0 | 388 | 991 |
| 6 | 982 | 521 | 1020 | 959 | 0 | 422 | 957 |
| 7 | 0 | 0 | 0 | 1660 | 1259 | 410 | 1496 |
| 8 | 1336 | 711 | 1020 | 956 | 0 | 408 | 989 |
| 9 | 2200 | 764 | 0 | 0 | 225 | 0 | 1050 |
| 10 | 0 | 0 | 0 | 2000 | 1800 | 0 | 398 |

WHAT IS CLAIMED IS:

1. A pipe capable of obtaining an F time in Jana Laboratories Procedure APTF-2 of at least 1000 hours, under the following conditions pH 6.8 (± 0.1); Chlorine 4.1 mg/L (± 0.1); Nominal ORP 830mV; fluid temperature 110°C (± 1); air temperature 110°C (± 1); pressure 70 psig (± 1); flow rate 0.1 Us gallons/min ($\pm 10\%$); said pipe comprising polyethylene having a density greater than about 0.925 g/cc.
2. The pipe of Claim 1 wherein pipe comprises an antioxidant system comprising two or more components.
3. The pipe of Claim 2 wherein one of the antioxidant system components provides extraction resistance and another provides oxidation resistance.
4. The pipe of Claim 3 wherein the antioxidant system includes two or more antioxidants selected from the group consisting of Irganox 1010; Irganox 1330; and Irganox 1076
5. The pipe of Claim 4 wherein the antioxidant system further comprises Irgafos 168.
6. A pipe comprising reactor grade polyethylene having a density greater than about 0.925 g/cc capable of obtaining an F time in Jana Laboratories Procedure APTF-2 of at least 1200 hours.
7. The pipe of claim 6 wherein the pipe further comprises at least one antioxidant effective for resisting chlorine and at least one additional antioxidant effective for resisting oxygen, wherein the antioxidants are resistant to extraction from the polyethylene resin by water.
8. The pipe of Claim 7 wherein the polyethylene is multimodal.
9. The pipe of Claim 7 wherein the density is greater than 0.940
10. The pipe of Claim 7 wherein the antioxidant effective for resisting chlorine is a hindered phenol.
11. The pipe of Claim 7 wherein the antioxidant effective for resisting oxygen is a hindered phenol.
12. The pipe of Claim 7 wherein the polyethylene resin further comprises one or more metal deactivators.
13. The pipe of Claim 7 wherein the polyethylene resin further comprises one or more phosphorous based stabilizer.

14. The use of a pipe as in Claim 7 for chlorinated hot water.
15. The pipe of Claim 1 in which the F time is greater than 1200 hours.

ABSTRACT OF THE DISCLOSURE

Stabilized polyethylene materials which offer an advantageously balanced combination of thermal, mechanical and processing properties, and which maintain their physical properties in chlorinated water environments are disclosed. The materials include an antioxidant system with components to provide extraction resistance in hot water environments and additionally provides oxidation resistance to both chlorine in the water interior of the pipe and oxygen in contact with the pipe's exterior.

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